Pyrite geochemistry as a recorder of early biosphere processes

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Pyrite (FeS_2) is abundant in Archean sedimentary rocks and provides an extensive archive of stable isotope data that has been used to support the early evolution of sulfur metabolisms on an anoxic early Earth. Both multiple sulfur (^{32}S, ^{33}S, ^{34}S, ^{36}S) and more recently iron (^{54}Fe, ^{56}Fe) stable isotopes can be measured by microanalytical techniques and coupled with trace element mapping to reveal multiple stages of pyrite precipitation. The development of these analytical methodologies has been important since pyrite was relatively stable under the anoxic conditions of the Archean (near-) surface environment where detrital reworking was common. Multiple stages of precipitation from diagenetic and metasomatic fluids may have led to modification and/or homogenization of potential isotopic biosignatures.

Here, we review a new and extensive database of pyrite SIMS Fe and multiple S isotope data from the Barberton Greenstone Belt, Southern Africa. Pyrite shows diverse and heterogeneous multiple S isotopes data that captured reduced and oxidized products from both atmospheric photolytic exit channels. Mixing between the two is common in pyrite populations and occurred either during diagenesis or metasomatic reworking. Mass-dependent overprinting indicates the early evolution of microbial sulfate reduction and elemental sulfur disproportionation. Fe isotopes record the Fe source that may have been variably affected by (microbial) Fe oxidation. Despite ferrous Fe-rich oceans, a considerable amount of the Archean pyrite data requires input of sedimentary Fe oxides. Abiotic fractionation during pyrite formation precludes identification of a role for disimilatory Fe reduction

The integration of isotope and chemical data with pyrite (internal) morphology, particularly the identification of tentative framboidal structures provides, despite uncertainties, relatively robust evidence for the rapid development of biogeochemical Fe and S cycling in the Paleoarchean. Pyrite can be interrogated as a ‘time capsule’ using multiple proxies that is not available with many other minerals.